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Patterning of Bi2Te3 Polycrystalline Thin-Films on Silicon

by Brian Morgan and Patrick Taylor

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14. ABSTRACT
Bi2Te3-based thermoelectric (TE) energy conversion devices are an attractive possibility for recovering usable energy from waste heat. The integration of TE devices on silicon substrates opens the door for new highly integrated systems where micro-electro-mechanical systems (MEMS) heat exchangers and sensor/actuator technology can be leveraged to improve conversion efficiency and system capability. One roadblock on this path is the development of reliable patterning methods for fabricating thin-film TE devices on silicon micromachined substrates. This report gives the results from investigating patterning techniques for polycrystalline Bi2Te3 films grown using molecular beam epitaxy (MBE). Lithographic patterning and both wet and dry etch techniques are discussed. Results show that the developed processes can be used to precisely pattern features smaller than 10 µm on a side and are scalable to vertical dimensions ($\gg$ or $\geq$) 10 µm.

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1. Introduction

Waste heat conversion is an area of significant interest to the Army, as >50% of the input energy to an internal combustion engine can be lost as heat. Should a fraction of this energy be recovered, significant benefits in power output and system efficiency could be realized. In their usual form, thermoelectric (TE) devices are fabricated from “bulk” materials that are synthesized by freezing molten boules forming ingots. Those ingots proceed through serial processes including saw-cut dicing, metallization, and soldering on the path towards a TE device. While bulk device fabrication is well-known and mature, miniaturizing that process for micromachined TE devices for small and/or complex systems becomes difficult given their limited size and serial manufacturing techniques. In contrast, micromachined TE generators could take advantage of the huge infrastructure that exists for parallel manufacturing of silicon-based microsystems to improve device yield, system performance, integration, and form factor. Applications such as unattended ground sensors, thermal imagers, or clandestine tagging, tracking, and locating (cTTL) are just some of the possible areas where this technology could be beneficial.

Industry demonstrations of thin-film TE devices include output powers of >14 W from a 4.6 cm^2 device at $\Delta T \sim 100$ °C, with reported efficiencies of 5–10% (*1*). However, TE materials are typically grown on expensive, exotic substrates like barium fluoride (BaF) or gallium arsenide (GaAs), neither of which is scalable compared to silicon, nor do they offer the ability to integrate electronic devices and/or sensors as silicon does. Thus, the goal of this research is to combine three areas of active research within the Microsystem thrust of the U.S. Army Research Laboratory (ARL) (TE materials, micro-electro-mechanical systems (MEMS) sensors/actuators, and thermal management) into a single-chip system similar to that shown conceptually in figure 1. This report details the technical progress and limitations of directly patterning TE thin-films on silicon for improved form factor, reduced system complexity, and superior thermal interfaces.

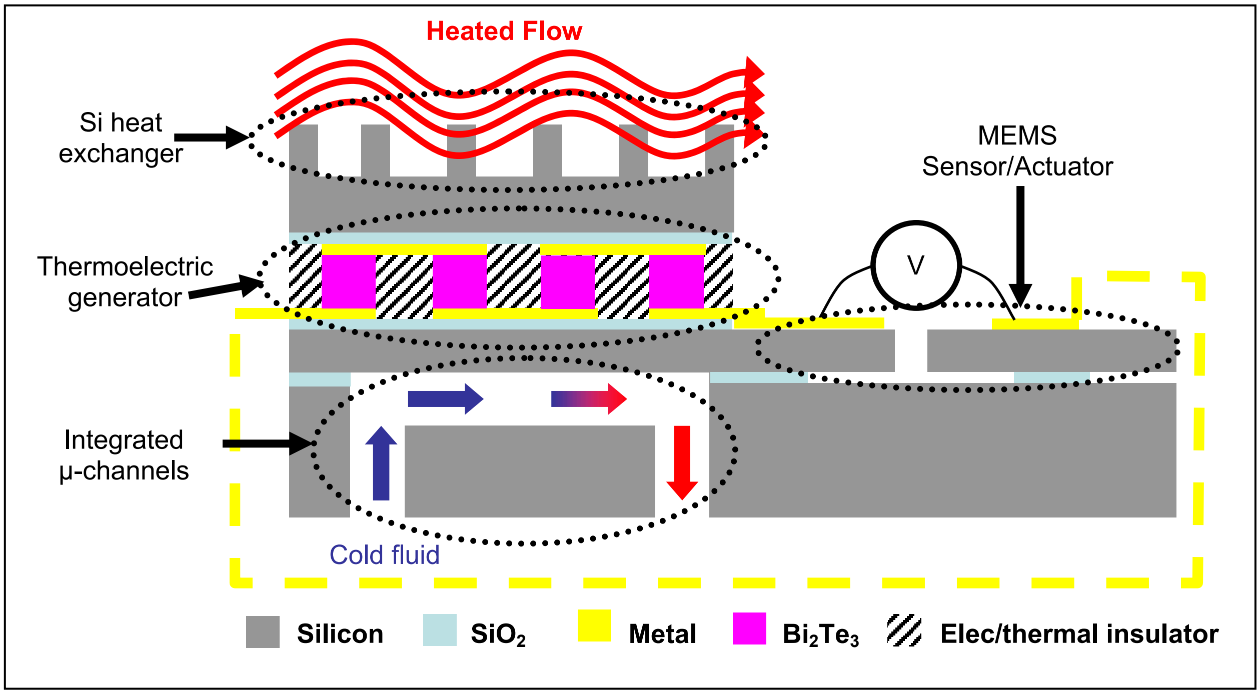


Figure 1. Conceptual schematic of a TE generator on silicon, where heat exchangers can be micromachined in silicon and integrated with MEMS sensors/actuators onto a single chip.

2. Sample Preparation

In general, when selecting a material for a TE device, one desires three characteristics: (1) high electrical conductivity to minimize electrical resistance losses, (2) low thermal conductivity to maximize the temperature gradient across the material, and (3) a high Seebeck coefficient to maximize the thermal voltage. These properties are typically expressed as the so-called "figure of merit (Z)" (*2*):

$$Z = \frac{\alpha^2 \cdot \sigma}{\kappa} \tag{1}$$

where α is the Seebeck coefficient (V/K), σ is electrical conductivity ($\Omega^{-1}m^{-1}$), and κ is thermal conductivity ($Wm^{-1}K^{-1}$). The figure of merit is plotted as a function of temperature in figure 2 (*2*). Given that many energy scavenging applications are in the near-room temperature regime (0–150 °C), bismuth telluride (Bi_2Te_3)-based materials offer the highest potential performance. Other efforts on lead-telluride (PbTe)-based materials for higher temperature applications are being pursued through a collaboration with the University of Florida (*3*).

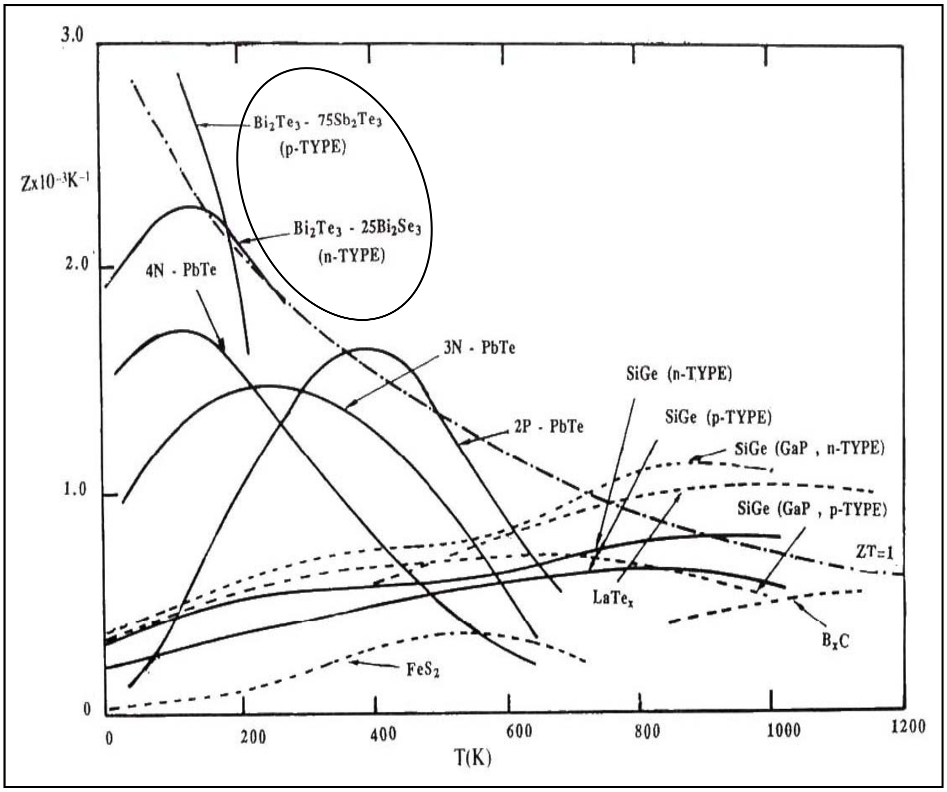


Figure 2. Figure of merit (Z) as a function of temperature for a variety of materials; for room temperature applications, Bi_2Te_3-based compounds are the obvious choice (*2*).

The samples used in this research started as 4-in <100> silicon wafers. A 1 µm thermal oxide was grown over the entire wafer to electrically insulate the TE device material from the silicon. Various metal pads were then defined using a standard lithography process (AZ5214) and lift-off in acetone (50 °C for 2 h). These patterned metal pads will eventually form bottom side interconnects between TE posts. After substrate cleaning in an RCA-1 bath to remove organic residue, the blanket Bi_2Te_3 films were grown using solid-source molecular beam epitaxy (MBE). As deposited, the films were undoped, and growth rates of ~1 µm/h were demonstrated. Thus far, films as thick as 9 µm have been achieved (reactor time limited), although there appears to be no upper limit to the thickness and thicker films are planned for future devices. After film growth, the sample is coated with a thin photoresist layer to protect the Bi_2Te_3 during a dicing step, in which 15 by 15 mm dies are separated for processing. The protective photoresist layer is removed in a PRS-3000 photoresist stripper for 2 min at 80 °C.

3. Photolithography

Before etching experiments could be undertaken, a photolithography step was used to create the appropriate pattern. Standard lithography recipes were adapted for this purpose. The best results were obtained using the following sequence: (1) spin coat AZ5214e at 1200 rpm for 30 s, (2) soft bake at 110 °C for 60 s, (3) contact exposure for 3.3 s, (4) reverse-image bake at120 °C for 30 s, (5) flood exposure for 5.5 s, and (6) develop for 60 s in AZ312MIF 1:1 DI. This resulted in a 2.8 μm thick photoresist layer in which features as small as 4 μm square were consistently defined. In general, the exposure times were the only parameters requiring significant attention, a fact largely attributed to the reduced reflectivity and increased light absorption of the polycrystalline Bi_2Te_3 surface compared to polished single crystal silicon.

The primary problem encountered during lithography was delamination during the development step. As shown in figure 3, on/around areas with pre-patterned metal pads, the Bi_2Te_3 adhered, while in open areas with only bare SiO_2 the film delaminated, likely from the lack of any chemical bonding to the surface. While figure 3 is an extreme case, such delamination is of little concern since most implementations will require metal underneath the Bi_2Te_3 post to serve as an electrical interconnect. In the future, the ability to grow single crystal Bi_2Te_3 directly on single crystal silicon may be investigated as an alternative means for improving film adhesion and doping at the expense of slightly more complicated system design.

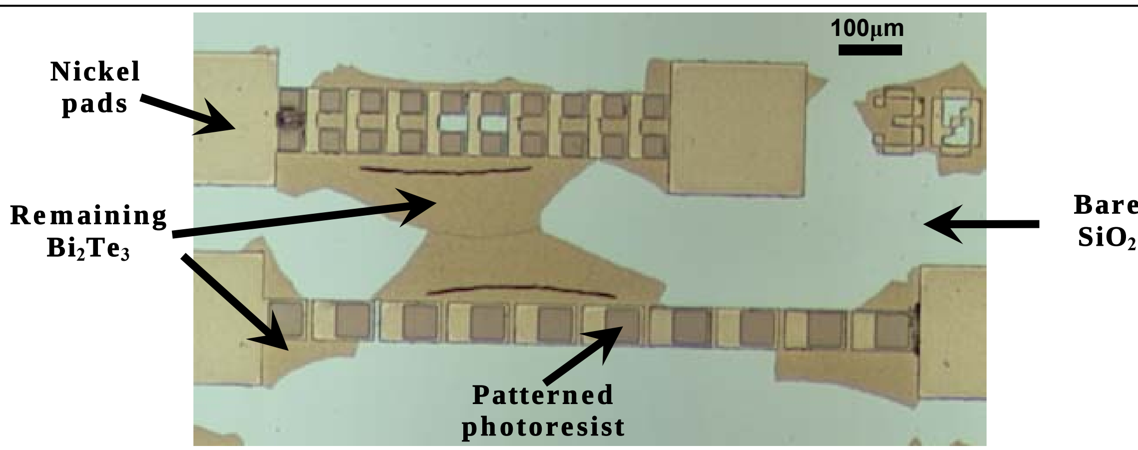


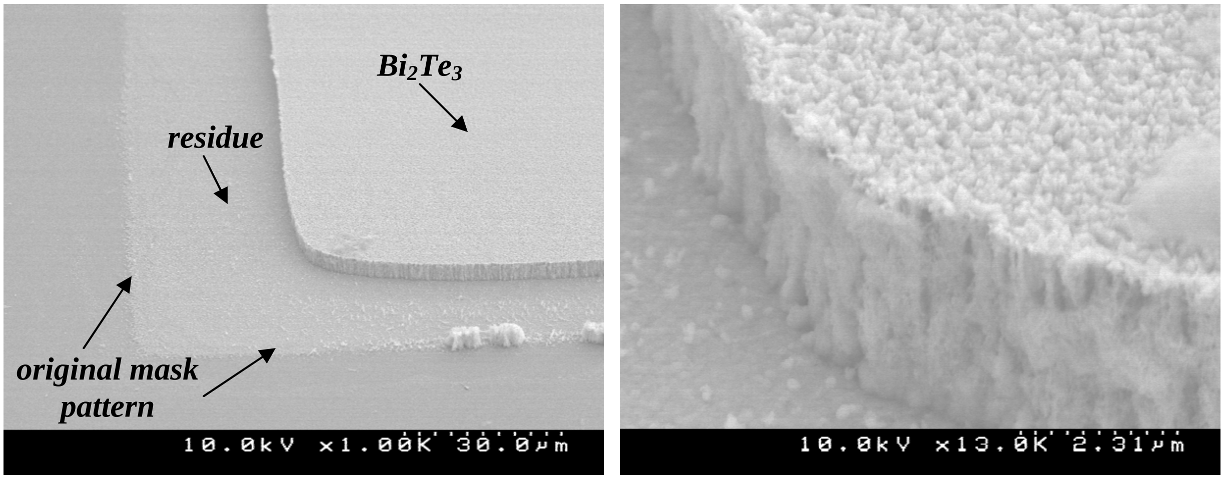
Figure 3. Optical micrograph of a Bi2Te3 sample after lithography—the patterned photoresist squares are nicely defined; however, the development step has caused significant delamination of Bi_2Te_3 where metal is not present to anchor it down.

4. Wet Chemical Etching

Wet chemical etching was first pursued due to its simplicity and availability. According to Dilberto et al. (*4*), a combination of hydrogen peroxide (H_2O_2), hydrochloric acid (HCl), and de-ionized water (DI) has proven effective at etching Bi_2Te_3-based compounds. However, particular attention should be given to the compatibility of wet chemical etchants with other materials on the wafer. In this case, the H_2O_2:HCl:DI mix is essentially a diluted form of the standard RCA-2 clean, which would etch both the Bi_2Te_3 device material as well as the metal pad. As an alternative, Shafai and Brett (*5*) used a diluted combination of HCl and nitric acid (HNO_3), a variant of the common "Aqua Regia." Since we desire to use photoresist as the masking material for process flexibility, we used a diluted version of Aqua Regia (3 HCl:1 HNO_3:2 DI) that according to Williams et al. (*6*) should not attack photoresist appreciably.

Vertical etch rates of ~0.5µm/min were achieved; however, the scanning electron microscope (SEM) images shown in figure 4 highlight that the horizontal undercut is >5 times the thickness. This fact indicates that there may be more exposed surface area in contact with the etchant because of, say, grain boundary effects and open voids within the material that causes the relatively fast lateral etch rate. While the grain structure and the presence of voids within the material can be improved in future growth studies, the best scenario for wet etching a polycrystalline material is still a 1:1 ratio of vertical to horizontal etch rates. Figure 4(a) also shows some residue that remained after the wet etch was performed. Energy-dispersive x-ray spectroscopy (EDX) analysis indicates this to be a carbon-based residue (*7*), likely from partial etching of the photoresist during immersion in the solution. Further dilution of the etchants could mitigate this effect (at the cost of etch rate), or the migration to a metal mask could be investigated.

Thus, while the wet approach offers reasonable etch rates (>0.5µm/min) and requires very simple bench-top equipment, wet patterning must be limited to low aspect ratio structures. Since TE generators perform most efficiently at high aspect ratios, an alternative technique is necessary to pattern smaller features.



(a) (b)

Figure 4. SEMs of wet etched Bi_2Te_3, showing (a) the large horizontal mask undercut and resulting residue that is quite evident and (b) a close-up of the resulting vertical sidewall.

5. Dry Plasma Etching

Dry plasma etching should provide the desired vertical etch characteristics; however, achieving significant etch rates and good selectivity to a photoresist mask is typically challenging. In addition, the capital equipment required is both complicated and expensive. For this work, we used an inductively coupled plasma (ICP) etch tool that allows independent tuning of the plasma density and ion energy. Literature reports show some success using common etch gasses (such as Ar, O_2, CH_4, etc.) with etch rates of ~60 nm/min (*4*). Combinations of CH_4-H_2 are often used for etching III-V devices in the same ICP chamber, and were therefore considered a good starting point. Each 15 by 15 mm die was mounted on bare 4-in silicon carrier wafers for handling by the system.

Using established recipes as a guideline, the initial experiments were focused on understanding the basic dependence of the Bi_2Te_3 etch rates in different gas mixtures and pressures. For the gas mixture, an initial combination of 10 sccm of CH_4, H_2, and Ar was compared to 15 sccm CH_4, 5 sccm H_2, and 15 sccm of Ar. In the latter mixture, it was expected that the increase in heavy Ar+ molecules bombarding the surface would promote ion-assisted etching, while an increase in CH_x radicals would increase chemical etching, leading to a dramatic increase in etch rate. The two pressure set-points were intended to investigate the tradeoffs between available etch species, average ion energy, and possible re-deposition of volatiles, all of which are known to affect the etch rate.

As shown in table 1, the initial recipe resulted in an etch rate of 0.22 µm/min, while changing the pressure and gas mixture successfully increased the etch rate to 0.66 µm/min, with pressure change having a greater influence than chemistry. This relatively high etch rate is important, because it represents a tenfold improvement over that reported in Dilberto et al. (*4*) and makes etching thick films (>10 µm) possible in realistic time. However, during this etch, we observed a selectivity of <5:1, meaning that the photoresist mask thickness must increase dramatically to etch thicker films, which in turn will reduce the resolution achievable in the resist. Therefore, a second round of experiments was devised to investigate improving the selectivity—a notoriously difficult property to control given that, for example, a change in ion energy effects the etch rates of both the Bi_2Te_3 and photoresist. We chose to vary the electrode power and pressure in an attempt to minimize ion bombardment on the photoresist while maintaining enough ion assisted etching of the Bi_2Te_3 to realize a significant overall etch rate. The gas combination of 15/5/15 was employed for all cases and the results are shown in table 2. For the case of higher electrode power (100 W), the low pressure had a slightly higher selectivity, but a vastly lower etch rate. For the lower electrode power (50 W), the etch rate decreased only slightly while the selectivity effectively doubled. Thus, a final etch rate >0.5 µm/min with selectivity well above 10:1 was achieved through simple changes in gas mixture, electrode power, and pressure. The initial and final etch parameters are shown in table 3.

Table 1. Measured etch rate (µm/min) as a function of chamber pressure and gas mixture (all at 100 W electrode power).

Gas Mix $CH_4/H_2/Ar$ (sccm)	**Pressure (mTorr)**	
	10	20
10/10/10	0.22	0.47
15/5/15	0.28	0.66

Table 2. Measured etch rates and selectivity to photoresist (PR) as a function of chamber pressure and electrode power (all using 15/5/15sccm of $CH_4/H_2/Ar$).

Etch Rate (µm/min) / Selectivity (Bi_2Te_3:PR)		**Pressure (mTorr)**	
		10	20
Electrode Power (W)	50	0.24 / 12.1	0.56 / 14.7
	100	0.28 / 6.5	0.66 / 5.0

Table 3. Initial and final etch recipe parameters.

	Coil Power (W)	Electrode Power (W)	Chamber Pressure (mTorr)	Gas Flow (sccm)		
				CH_4	H_2	Ar
Initial	600	100	10	10	10	10
Final	600	50	20	15	5	15

SEM images of prototype TE posts on patterned metal features are shown in figure 5. Note the lack of residue and vertical sidewall profiles achieved, establishing this etching technique as a viable tool for fabricating micromachined TE legs. The developed techniques should enable scaling of similar structures to even thicker films, enabling improved performance of waste heat recovery systems.

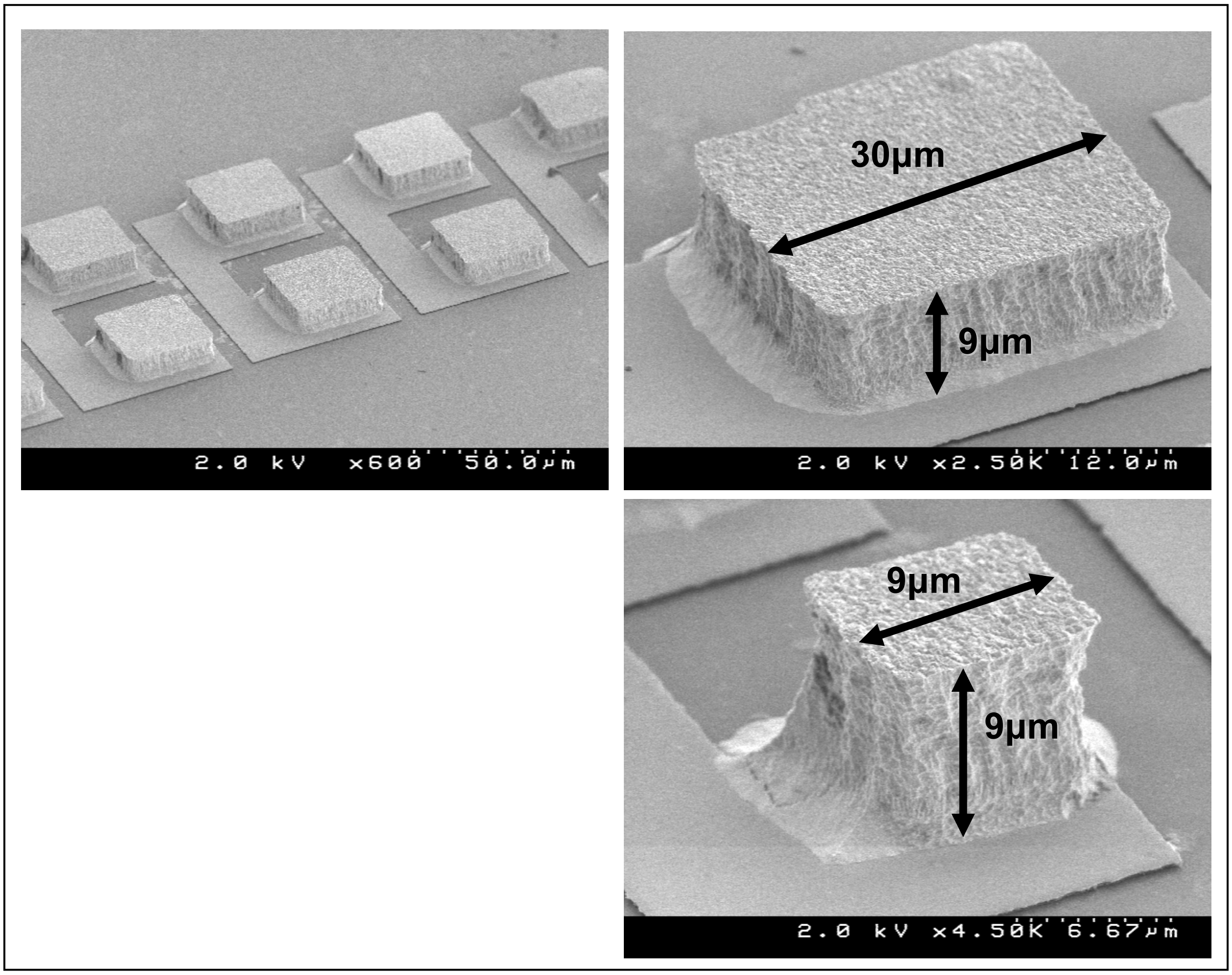


Figure 5. SEMs of etched Bi_2Te_3 posts on pre-patterned metal pads—note lack of residue on metal as well as the verticality of the sidewalls.

6. Conclusion

This research has demonstrated that Bi_2Te_3-based TE materials and devices can be monolithically integrated with silicon-based materials and MEMS most efficiently provided there is an "adherent" on the SiO_2 surface. For this work, a base metal is highly successful and necessary for eventual device fabrication anyway. These Bi_2Te_3 TE thin-films can be reliably patterned using the existing, large technology infrastructure available within silicon processing facilities. Experiments have shown that high etch rates (>0.5 μm/min) and photoresist selectivity (>10:1) can be achieved through straight-forward process modifications. Future work will concentrate on using these fabrication techniques to create characterization structures in order to measure and optimize the TE properties of these films.

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Acronyms

ARL	U.S. Army Research Laboratory
BaF	barium fluoride
Bi_2Te_3	bismuth telluride
cTTL	clandestine tagging, tracking, and locating
DI	de-ionized
EDX	energy-dispersive x-ray spectroscopy
GaAs	gallium arsenide
H_2O_2	hydrogen peroxide
HCl	hydrochloric acid
HNO_3	nitric acid
ICP	inductively coupled plasma
MBE	molecular beam epitaxy
MEMS	micro-electro-mechanical systems
PbTe	lead-telluride
SEM	scanning electron microscope
TE	thermoelectric

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